# THE SURFACE AREA AND SORPTION.

By Michael TARLÉ.

Received July 22, 1927. Published September 28, 1927.

In the " Bulletin of the Chemical Society of Japan "[1] appeared an interesting report by Prof. Jitsusaburo Sameshima under the title: " The Sorption of Gas by Charcoal as a Dissolution Phenomenon." Prof. Sameshima made measurements of amounts of carbon dioxide absorbed by various kinds of charcoal (activated in the same way), and found, that the amounts absorbed are independent of the area of the surface of the charcoal; therefore he considers the phenomenon of sorption not as a condensation of gas on the surface, but as a dissolution of the gas in the charcoal. In my opinion this deduction is based on misunderstanding: the interesting experiments of Prof. Sameshima do not prove the correctness of his point of view.

1. It is not quite clear in what way has been the amount of absorbed gas measured. The experimental part has been probably described in the former publications of Prof. Sameshima, which are inavailable for me at present. So far one can judge the volume absorbed has been measured indirectly and the measurements are partly based on the knowledge of the volume of the charcoal; this volume is calculated under assumption that the density of the charcoal is 2.1. This assumption might be correct for highly active charcoals only; in other words for charcoal, which has been heated for a rather long period of time (6 to 24 hours) at a temperature of 800–1000°C if, and as in experiments under discussion, has not been treated by chemical agents. Now, it is highly probable that being activated in this way, the raw charcoal changes its former structure and passes from the amorphous state to cristallinic (graphite). During this transition period —possibly under the influence of unsaturated atoms[2]—the charcoal has a high absorbing capacity. After the transition is finished and the whole of the charcoal is changed to graphite, the high active properties disappear. The process of transition can be followed by measurements of the true density of the charcoal, as has been shown by me in a paper submitted to the Anti-Gas Branch of the Chemical Warfare Department in London in 1918. I repeated now some of those measurements at the Research Laboratory of the Moukden Arsenal (in connection with an investigation of the velocity of sorption problem, soon to be

(1) This journal **2** (1927), 1.
(2) O. Ruff, *Z. angew. Chem.*, **38** (1925), 1164.

published) and again found that the true density is a function of the duration and temperature of the activation process and is closely connected with the absorbing capacity. Different kinds of charcoal (of different origin and of different kind of activation) showed following results:

| No. | Absorbing capacity for chlorine (%) $A$ | True density[1] $D$ | Volume of the pores per 1 gr. $C$ | $\frac{A}{C}$ |
|---|---|---|---|---|
| 1 | 11.1 | 1.44 | — | — |
| 2 | 23.0 | 1.52 | 1.18 | 19.3 |
| 3 | 32.2 | 1.94 | 0.96 | 33.5 |
| 4 | 36.6 | 1.43 | 1.30 | 27.1 |
| 5 | 38.5 | 1.91 | 1.15 | 33.5 |
| 6 | 40.1 | 2.10 | 1.32 | 30.6 |
| 7 | 52.0 | 1.84 | 1.79 | 29.1 |

We see from this table that in only one case has been the density 2.1. As Prof. Sameshima activates his charcoal only *one* hour at 800°C. we may assume that its density has been lower than 2.1 (probably 1.7–1.9) and therefore the amounts of the absorbed gas (the absorbing capacities) are not represented quite correctly by the figures of Prof. Sameshima. The correction will vary with the kind of charcoal used and, although not a large one, may change the opinion "that the amounts of absorbed carbon dioxide... by various kinds of charcoals are nearly equal in each other." Furthermore we see from the above table that the rate "$A : C$" is nearly constant and from this we may assume, that —at least in some cases— the absorbing capacity is nearly proportional to the volume of the pores and therefore cannot be explained by the dissolution theory of Prof. Sameshima. His statement, that ".. It is not conceivable that different materials give the charcoals of nearly same surface area.." is also contradicted by facts. The activation process changes the original wood structure, the original difference of the structure with the progressing process disappears, the final density becomes about 2.1, the charcoal assumes the structure of the graphite. So the surface area (after activation) will depend not so much on the original structure, as on the method of activation. As the charcoals in the experiments of Prof. Sameshima has been activated in the same way the total absorbing capacity will not differ much from each other.

2. The second important point of the investigation of Prof. Sameshima is "that the absorbed amounts by the granular and by the powder charcoal are the same. ... The dissolved (absorbed ? M.T.) quantity of gas depends

(1) These density figures are not absolutely correct, as we do not know the density of the liquid which filled the micropores and is compressed; but the volume of the micropores is evidently small comparing with the volume of the macropores. The mistake is also of a small order. See the investigation by Harkins and Ewing, *J. Am. Chem. Soc.*, 43 (1921), 1790.

only upon the amount of charcoal, and does not depend upon the surface area of it." This point is surely based on a misunderstood conception of the surface area of an absorber. The experimental method of Prof. Sameshima has been as follows. The amount of the gas absorbed by granulated charcoal has been measured, then the charcoal powdered (in a mortar, by hand), the charcoal heated, the gas removed, and the charcoal again brought in contact with gas. The first measurement of the absorbed amount gives practically the same result as the second one, and from this Prof. Sameshima concludes that the absorbing capacity is independent of the surface area, because the surface area of a powder is, in his opinion, much larger than that of the granules. This conclusion is incorrect, because for a very porous body both areas will be practically equal.[1] The surface area of a porous body consists of two areas: area of the external surface and that of the internal surface (interface), i.e. the surface of the macro- and micropores.[2] The second area is of another order of magnitude and incomparably larger than the first one; therefore the changing of the first area will have no practical influence upon the second one, which is not changed by grinding.

Let us make the following calculation. We take one piece of charcoal, a cube of 1 c.c., with an outside surface of 6 sq. cm. We do not know accurately the internal surface area; Lamb[3] assumes that it is equal to 100 sq. meters for 1 gr. of charcoal; Cude and Hulett[4] found it to be about 200 sq. meters; from the study of microphotograms taken at the Central Scientific Laboratory of the Russian War Office during the European war[5] I found the area of the macropores only to be about 10 sq. meters for 1 gr. of activated charcoal. If we take even this low figure as a base of our calculation and assuming that the apparent density is 0.5 we get for the total area—both external and internal—of our cube $6+50000=50006$ sq. cm. Now let us grind the charcoal. If we break it to 10000 small particles, each particle having a volume of 0.0001 c.c., the external surface of each particle will be $0.002116\times 6=0.0127$ sq. cm. As we have 10000 such particles the external area will be equal to 127 sq. cm., and the total area will be $50000+127=50127$. So the change of the area produced by grinding equals to 0.2% of the area only. In other words the powdering produces a negligible effect upon the surface area and therefore the experiments of Prof. Sameshima do not prove the correctness of the dissolution theory.

Manchurian Arsenal, Moukden, China.

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(1) Cude and Hulett, *J. Am. Chem. Soc.*, 42 (1920), 398.
(2) Harkins and Ewing, *J. Am. Chem. Soc.*, 43 (1921), 1798.
(3) *J. Am. Chem. Soc.*, 42 (1920), 1146.
(4) Loc. cit.
(5) Prof. Chlopine, "The Foundations of the Anti-Gas Defence." Petrograd (Leningrad), 1926.

# ON DR. TARLÉ'S PAPER ENTITLED "THE SURFACE AREA AND SORPTION."

By Jitsusaburo SAMESHIMA.

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I am glad to know that my paper under the title "The sorption of gas by charcoal as a dissolution phenomenon," which was published in the January number of this journal, has been read and criticised by Dr. Tarlé.[1] I can reply at once to the kind criticism of Dr. Tarlé.

1. In the first place, the method of measurement of the amount of absorbed gas was described in my paper (pages 2, 3 and Fig. 1). But I will explain it here again :—

Exactly weighed charcoal (evacuated, sealed in a tube and weighed) was put in the bulb A (cf. Fig. 1 in the paper cited above), and then evacuate the bulb A and the burette E. Close the cock B, introduce the carbon dioxide gas into the burette E and then close the cock D. Read the volume of the gas in the burette E after adjusting the pressure by the mercury reservoir G. Now open the cock B. Then the gas enters into the bulb A and is absorbed by the charcoal. The absorbed amount of gas can be traced time to time by reading the burette E. The final amount of absorption is known also by reading the burette E after sufficiently long time.

Now the absorbed amount of gas can be calculated as follows :—

$$V = v - v' - v'',$$

where $V$ denotes the volume of gas absorbed by the charcoal taken,

$v$, the volume of gas introduced into the burette E,

$v'$, the volume of gas remaining unabsorbed in the burette E.

$v''$, the volume of gas remaining unabsorbed in the bulb A.

The temperature and the pressure of the gas in various parts of the apparatus must, of course, be reduced to the same conditions, say 0°C. and 760 mm. The value of $v''$ can be obtained by the formula,

$$v'' = (a - c)\frac{273.1P}{760T},$$

(1) Former article in this journal.

where $a$ denotes the capacity of the bulb A,
$c$, the volume of the charcoal,
$P$, the pressure of the gas,
$T$, the temperature of the gas in the bulb A.

Thus $(a-c)$ is the free space in the bulb A. A few of the actual data of observations are given in the following table (cf. Table 1 and Table 2 of the paper cited above).

| | Time | | $v$ c.c. | $v'$ c.c. | $a$ c.c. | Wt. of charcoal gr. | $c$ c.c. | $c''$ c.c. | $V$ c.c. | Absorb. vol. for 1 gr. c.c. |
|---|---|---|---|---|---|---|---|---|---|---|
| | min. | sec. | | | | | | | | |
| Granular charcoal. (third series) | — | 15 | 53.200 | 19.071 | 6.046 | 0.8604 | 0.4097 | 5.220 | 28.909 | 34.382 |
| | — | 61 | „ | 9.756 | „ | „ | „ | 5.266 | 38.178 | 44.372 |
| | 4 | 25 | „ | 6.041 | „ | „ | „ | 5.165 | 41.994 | 48.808 |
| | 40 | 0 | „ | 3.489 | „ | „ | „ | 5.164 | 44.547 | 51.775 |
| | 79 | 0 | „ | 2.930 | „ | „ | „ | 5.164 | 45.106 | 52.424 |
| | 365 | 0 | „ | 2.150 | „ | „ | „ | 5.164 | 45.886 | 53.331 |
| | 3205 | 0 | „ | 1.550 | „ | „ | „ | 5.164 | 46.486 | 54.028 |
| Powder charcoal. | — | 22 | 53.837 | 9.697 | 6.046 | 0.8752 | 0.4168 | 5.158 | 38.982 | 44.540 |
| | — | 57 | „ | 6.031 | „ | „ | „ | 5.158 | 42.648 | 48.729 |
| | 5 | 8 | „ | 3.398 | „ | „ | „ | 5.158 | 45.281 | 51.738 |
| | 41 | 0 | „ | 2.197 | „ | „ | „ | 5.157 | 46.483 | 53.111 |
| | 100 | 0 | „ | 2.006 | „ | „ | „ | 5.158 | 46.673 | 53.329 |
| | 295 | 0 | „ | 1.814 | „ | „ | „ | 5.158 | 46.865 | 53.548 |
| | 3110 | 0 | „ | 1.443 | „ | „ | „ | 5.157 | 47.237 | 53.972 |

In this table the values of $c$ (0.4097 and 0.4168) have been computed by the assumption that the density of charcoal is 2.10. Dr. Tarlé does not mention on the paper of Howard and Hulett.[1] It seems that their results are more trustworthy than any other density determinations ever published. They obtained the value 2.05–2.28 for the densities of various kinds of activated charcoals.

If we assume, however, the density to be 1.7 as Dr. Tarlé's opinion, then the values of $c$ increase to 0.506 and 0.515 c.c. respectively. Accordingly $V$ take lower values by 0.096 and 0.098 c.c. respectively than the values given in the table, which are 0.2% of the values of $V$. Then the absorbed volume of carbon dioxide by 1 gram of sugar charcoal at 25°C. and under 760 m.m. becomes 53.9 c.c. instead of 54.0 c.c. This is but small difference.

At any way, the question on the density of charcoal gives no serious effect on my result. My result are always referring to 1 gram of charcoal,

(1) Howard and Hulett, *J. Phys. Chem.*, **28** (1924), 1088.

not 1 cubic centimeter of it. So the error which might come from the uncertainty of the density of charcoal is less than 0.2% in the final results. And in the comparison of the absorption velocities by granular and by powder charcoals, this uncertainty gives entirely no effect on the results, because the amounts of charcoals used are always nearly equal in granular and in powder ones.

The "activation," in my opinion, is nothing more than the purification process of the impure charcoal. This is analogous to the fact that the purified water dissolves much hydrochloric acid gas than the impure water. The ordinary charcoal contains much organic matters as well as inorganic "ash." These impurities can be removed by heating in the steam or in the air, or treating with chemicals etc. The amounts of impurities, however, can by no means be estimated by the elementary analysis. The surface area may somewhat increase by the partial oxidation of the charcoal, and this may result the increasing of the absorption velocity of gas in the "break point" experiment.(1)

Dr. Tarlé measured the volume of pores of charcoals. I do not know how these volumes were computed, but if he obtained these volumes from the differences of true densities and block densities (i.e. apparent densities), then it is almost meaningless to compare them with the absorption capacities. There is no relation between the surface area and the volume of pores which have been computed in such a manner. The surface area may depends upon the average volume of individual pore, but not the total volume of pores.

The charcoal probably changes its structure from amorphous to crystallinic by prolonged heating to the temperature higher than 1000°C., and this results the diminution of the absorption capacity of gas as was already described in the former paper (page 9).

2. It is true that the charcoal has a great numbers of small pores. But the surface area of it must, certainly, increase by grinding. In Dr. Tarlé's calculation, he considered that one cubic centimeter of charcoal produce 10000 particles by grinding. Then assuming the particles are cubic in form, the length of one side of these particles becomes, in average, 0.46 mm. This is evidently far from the truth. I have examined my powdered charcoal microscopically, and known that the particles range from 0.01 mm. down to those smaller than the lower limit of microscopical observation. Let us assume that the average length be 0.001 mm., then the number of particles derived from one cubic centimeter of charcoal is $10^{12}$. Accordingly, the sum of the surface areas of these particles is, $6 \times 0.001^2 \times 10^{12} = 6 \times 10^6$ sq.

(1) Chaney, Ray and John, *Ind. Eng. Chem.*, 15 (1923), 1244.

mm.=6 sq. meter. If we assume that the total area of one gram of charcoal be 100 square meters,[1] and the block density of it be 0.5, then the increase of area by grinding amounts to 12% of the total area. The increase of area by grinding of the porous substance is less than that by grinding of the compact substance. So the above figure must be lowered to 6% or so. This is far above the experimental error of the determination of absorption capacity. In the present study, the experimental error is 0.2%. Even if the length of the particles be 0.01 mm. in average, the increase in area becomes to 0.6%, which still beyond the experimental error. Therefore the adsorption amount must increase by grinding if the adsorption theory be true.

The idea that the gas molecules condense on the surface of charcoal is merely a hypothesis. It is more natural, I think, to consider the absorption of gas by charcoal is caused by the dissolution than by the adsorption. There are numerous examples of absorption of gases by solid substances which can be explained by dissolution or compound forming theory, that is one phase theory, namely, the absorption of hydrogen by palladium, oxygen by silver, and hydrogen, carbon dioxide or water vapour by rubber etc.

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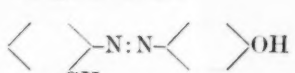
## SPECTROCHEMICAL STUDIES OF HYDROXYAZO-COMPOUNDS. PART V.[2]

By **Taku UEMURA** and **Shozo TABEI.**

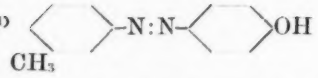
Received June 11, 1927. Published September 28, 1927.

Some influences with regard to the methyl-group in toluneazo-cresols were mentioned in our previous paper,[3] and, in this paper, we shall continue the same subject.

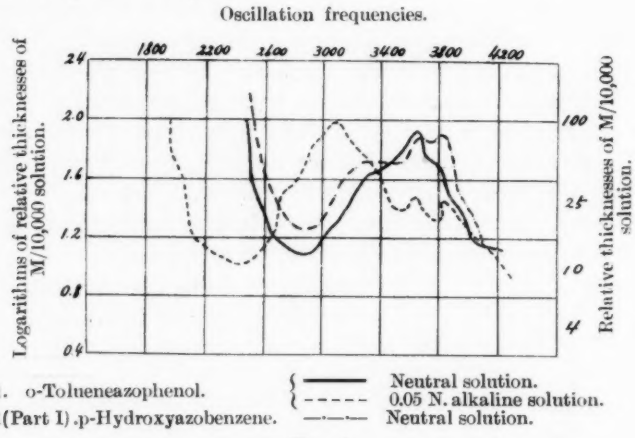
### Experimental.

1. **o-Toluneazophenol,**[4] 

(1) Lamb and Coolidge, *J. Am. Chem. Soc.*, **42** (1920), 1168.
Garner, McKie and Knight, *J. Phys. Chem.*, **31** (1927), 641.
(2) Read before the Chemical Society of Japan, June 11, 1927.
(3) Uemura and Tabei, This journal, **2** (1927), 229.
(4) Noelting and Werner, *Ber.*, **23** (1890), 3257; Paganini, Ibid. **24** (1891), 366.

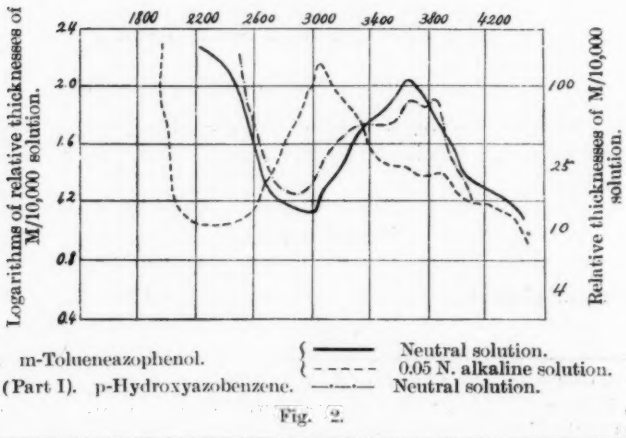
2. **m-Toluneazophenol,**[1] 

The neutral solutions of these two compounds are yellow and give a deeper shade by adding KOH. When we compare the neutral absorption curve of p-hydroxyazobenzene[2] with the absorption curves of these compounds, the hyperchromic influence due to the methyl-group can be distinctly observed (Fig. 1 and Fig. 2).




1. o-Toluneazophenol. { ——— Neutral solution. - - - - 0.05 N. alkaline solution.
1(Part I) .p-Hydroxyazobenzene. —·—·— Neutral solution.

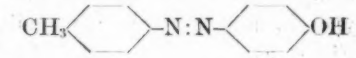
Fig. 1.




2. m-Toluneazophenol. { ——— Neutral solution. - - - - 0.05 N. alkaline solution.
1 (Part I). p-Hydroxyazobenzene. —·—·— Neutral solution.

Fig. 2.

(1) Paganini, *Ber.*, **24** (1891), 368.
(2) This journal, **1** (1926), 262.

3. **p-Toluneazophenol,**[1] 

The absorption curves of this compound (Fig. 3) are slightly hypochromic than those of the previous two compounds. But, comparing the curve of p-hydroxyazobenzene[2] with these, we can observe an effect similar to the one we found in the cases of the two above-mentioned compounds.

The colour of this alkaline solution is orange of a somewhat deeper shade than No. 1 and No. 2. By the addition of alkali, only a bathochromic effect can be shown in the absorption curves of these three toluneazophenols.

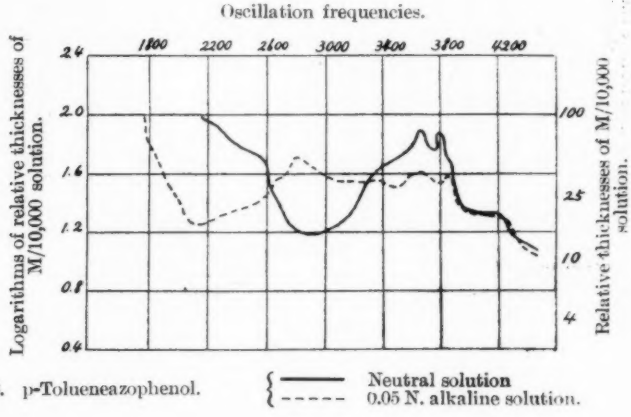
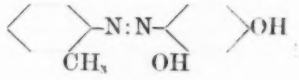
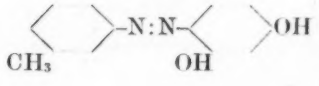
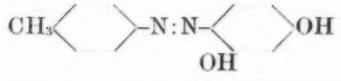



Fig. 3.

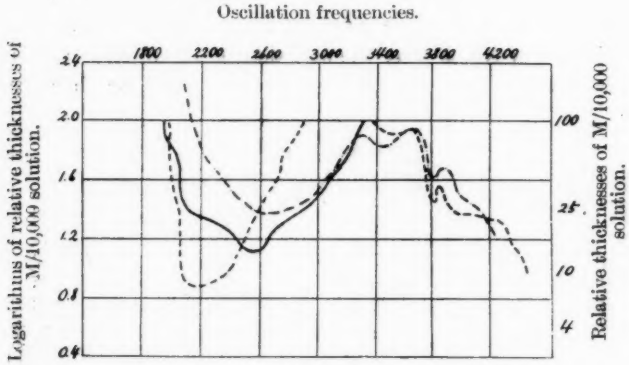
4. **o-Toluneazoresorcinol,**[3] 

5. **m-Toluneazoresorcinol,**[4] 

6. **p-Toluneazoresorcinol,**[5] 

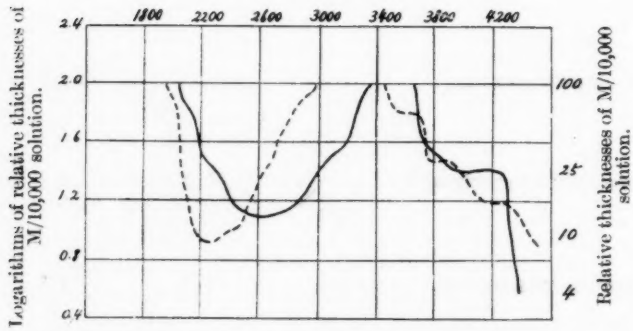
(1) Heumann and Oeconomides, *Ber.*, **20** (1887) 905; Kimich, Ibid., **8** (1875), 1030.
(2) Loc. cit.
(3) Wallach and Fischer, *Ber.* 15 (1882), 2825.
(4) Obtained from m-toluidine and resorcinol.
(5) Wallach, *Ber.*, **15** (1882), 2821.

These three compounds hardly produce any change in colour through alkali, and the hyperchromic influence can easily be recognised in their absorption curves (Fig. 4, Fig. 5 and Fig. 6). The hyperchromic effect due to the methyl-group may be detected in comparing it with benzeneazoresorcinol[1] (Fig. 4).




4. o-Tolueneazoresorcinol. { ——— Neutral solution. ----- 0.05 N. alkaline solution.
2 (Part 1). Benzeneazoresorcinol. —·—·— Neutral solution.

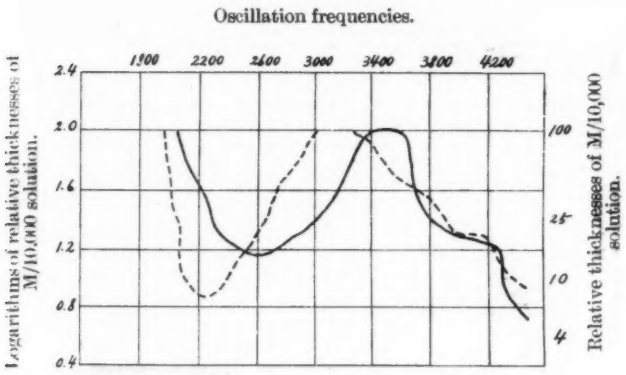
Fig. 4.




5. m-Tolueneazoresorcinol. { ——— Neutral solution. ----- 0.05 N. alkaline solution.

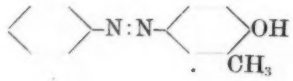
Fig. 5.

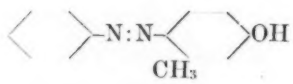
(1) This journal, 1 (1926), 262.




6. p-Tolueneazoresorcinol. { ——— Neutral solution. ----- 0.05 N. alkaline solution.

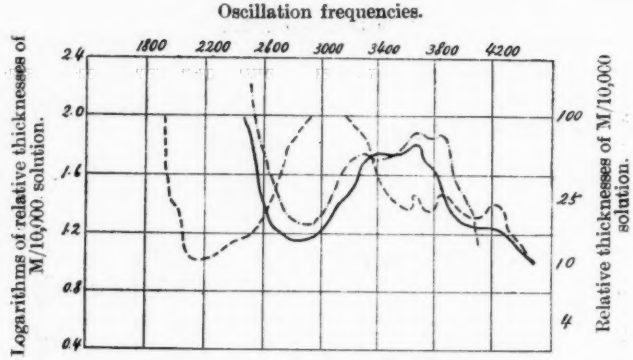
Fig. 6.

7. Benzeneazo-o-cresol,[1] 

8. Benzeneazo-m-cresol,[2] 

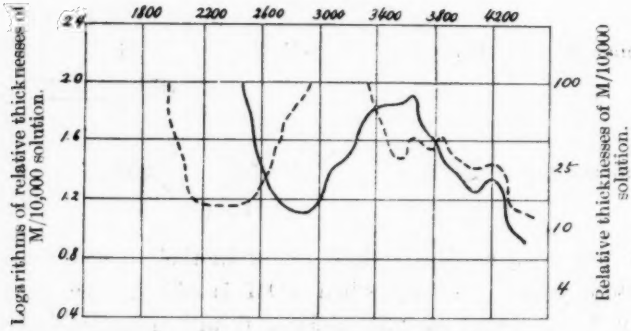
These two compounds are light yellow in their neutral solution and change into a yellowish orange when KOH is added. Their absorption curves (Fig. 7 and Fig. 8) are quite different from benzeneazo-p-cresol,[3] and this must be owing to the position of the hydroxyl-group in the cresol ring. When it takes the para-position with respect to the azo-group (these two compounds), only one absorption band can be seen, while two bands are clearly represented in the case of the ortho-position (benzeneazo-p-cresol). Comparing these absorption curves with that of p-hydroxyazobenzene[4] (Fig. 7), we are able to find the hyperchromic influence which most likely comes from the methyl-group in the cresol ring.

(1) Liebermann and Kostanecki, *Ber.*, 17 (1884), 131 & 879.
Noelting and Kohn, Ibid., 17 (1884), 363.
(2) Noelting and Kohn, Ibid., 17 (1884), 366.
(3) This journal 1 (1926), 263.
(4) Loc. cit.



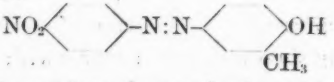

7. Benzeneazo-o-cresol. { ——— Neutral solution. ----- 0.05 N. alkaline solution.
1 (Part I). p-Hydroxyazobenzene. —·—·— Neutral solution.

Fig. 7.



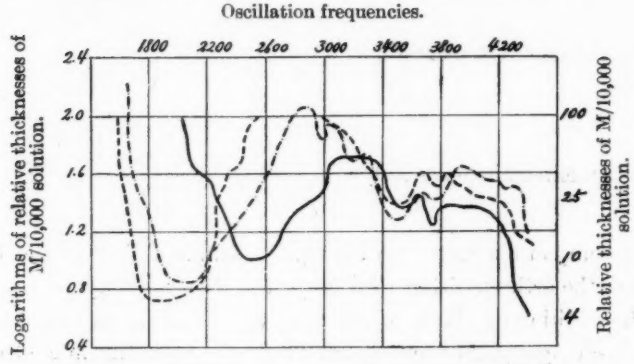

8. Benzeneazo-m-cresol. { ——— Neutral solution. ----- 0.05 N. alkaline solution.

Fig. 8.

**9. p-Nitrobenzeneazo-o-cresol,**[1] 


The yellow neutral solution changes into deep red when it is alkaline, but can not turn blue. When we compare the alkaline solution curve (0.002 N. KOH) of p-nitrobenzeneazophenol[2] with the curve of this compound (Fig. 9), the hyperchromic effect due to the methyl-group can be recognised.

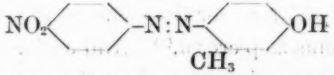
(1) Bamberger, *Ber.*, **28** (1895), 846.
(2) This journal, 1 (1926), 263.



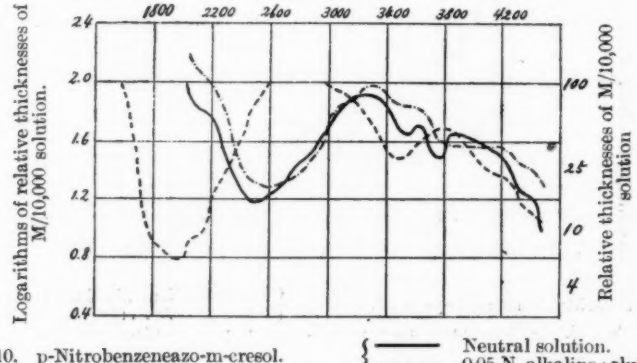

9. p-Nitrobenzeneazo-o-cresol. { ——— Neutral solution.
- - - - - 0.002 N. alkaline solution.
4 (Part I). p-Nitrobenzeneazophenol. —·—·— 0.002 N. alkaline solution.

Fig. 9.

10. **p-Nitrobenzeneazo-m-cresol,**[1]




The colour change through alkali is just the same as No. 9 compound. This neutral curve (Fig. 10) is slightly more hyperchromic than that of p-nitrobenzeneazophenol.[2] As the nitro-radical is situated in the para-position with regard to the azo-group, hyperchromic and bathochromic influences somewhat greater than No. 7 and No. 8 compounds are observed in the absorption curves of No. 9 and No. 10 compounds.

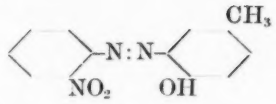



10. p-Nitrobenzeneazo-m-cresol. { ——— Neutral solution.
- - - - - 0.05 N. alkaline solution.
4 (Part I). p-Nitrobenzeneazophenol. —·—·— Neutral solution.

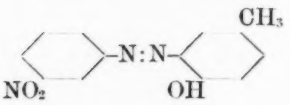
Fig. 10.

(1) Bamberger, *Ber.* 28 (1895), 847.
(2) Loc. cit.

11. o-Nitrobenzeneazo-p-cresol,[1]




12. m-Nitrobenzeneazo-p-cresol,[2]




These componnds have two absorption bands owing to the hydroxyl which takes the ortho-position with respect to the azo-group.

By the addition of alkali to their neutral solution, the colour of these compounds changes yellow into red and only the bathochromic effect can be detected in their absorption curves, not the hyperchromic, like No. 9 and No. 10 compounds. This means probably that the hydroxyl situated in ortho-position with respect to the azo-group is less effective than the one in para-position, for the same relation is also preserved in the curve of p-nitro-benzeneazo-p-cresol.[3] And as for the nitro-radical, we may obtain a greater bathochromic curve when the para-position with regard to the azo-group is occupied by that group (Fig. 11 and Fig. 12).

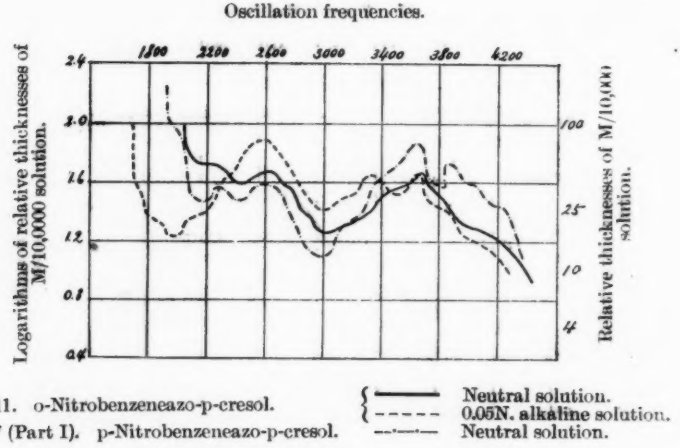



Fig. 11.

(1) Goldschmidt and Brubacher *Ber.* **24** (1891), 2308.
(2) Meldola and Hanes *J. Chem. Soc.*, **65** (1894), 838.
(3) This journal. **1** (1923), 265.

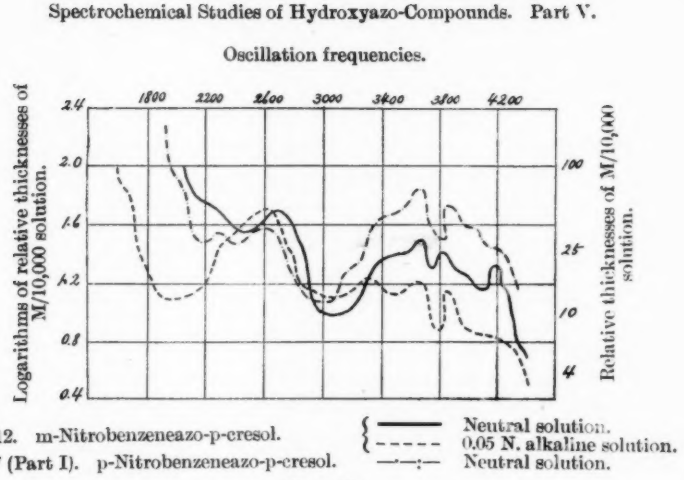



Fig. 12.

## Summary.

(1) Tautomeric transformations may take place in these hydroxyazo-compounds.

(2) We may assign A (azo)-form[1] to the neutral solution and R (red)-form[1] to the alkaline.

(3) In general, one band can be shown in the absorption curves, except when the hydroxyl-group takes an ortho-position with regard to the azo-group.

(4) Hydroxyl- and nitro-radicals in para-position with respect to the azo-group are most effective in the absorption curve.

(5) The methyl-group has generally a hyperchromic influence upon the non-methylated compounds.

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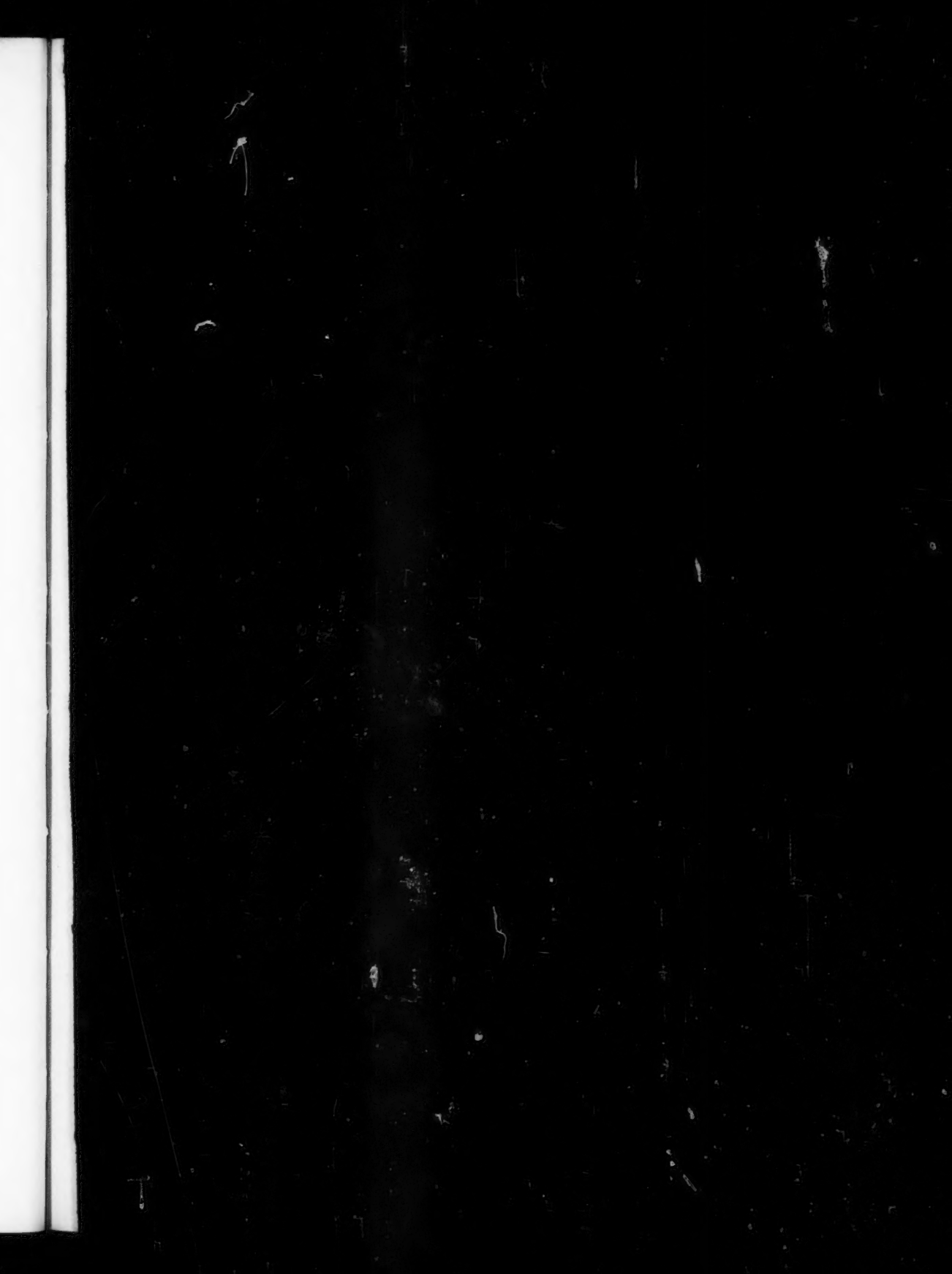
Dyeing Department, Tokyo Higher Technical School.

(1) This journal, 1 (1926), 261.